

PATENT SPECIFICATION

751600



Date of Application and filing Complete Specification May 7, 1954.

No. 13472/54.

Application made in United States of America on June 30, 1953.

Application made in United States of America on June 30, 1953.

Complete Specification Published June 27, 1956.

Index at acceptance:—Classes 81(1), A; 96, B(3A:31); 100(2), CA13; and 100(4), H.

COMPLETE SPECIFICATION

Microscopic Oil-Containing Capsules and method of making them

We, THE NATIONAL CASH REGISTER COMPANY, of Dayton, in the State of Ohio, and Baltimore, in the State of Maryland, United States of America, a Company incorporated under the laws of the State of Maryland, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to microscopic oil-containing capsules of gelled hydrophilic colloid material and to a method of making them by coacervation.

Thus, according to the invention, there is provided a microscopic oil-containing capsule wherein the casing thereof includes a gelled hydrophilic colloid material formed around oil droplets by coacervation.

According to a further feature of the invention there is provided a method of producing microscopic oil-containing capsules wherein two substances, one of which is a gellable hydrophilic colloid material and capable of producing coacervates when mixed with the other substance, are brought into contact in the presence of the oil such that when coacervation occurs, the gelled hydrophilic colloid material is formed around droplets of the oil to form capsules, and wherein the said colloid material is subsequently gelled.

In one embodiment of the invention the capsules are oil-droplet-containing cases of complex colloid material, and are formed by causing deposition of complex colloid material around microscopic oil droplets by a process of causing coacervation to occur in a mixture of two colloid sols in which the oil droplets are suspended, and then gelling the complex colloid.

The mixture may be made by forming an aqueous sol of one colloid, emulsifying the selected oil therein, and mixing the emulsion with an aqueous sol of the

other colloid, or the two sols may be made and mixed and the oil emulsified therein.

The coacervation is caused by dilution and/or by adjusting the pH of the mixture. The colloid materials used in the sols must be ionizable and exist in the mixture with different ionic charges. This may be brought about by selection of the colloid materials or by adjusting the pH of the sol mixture in which the oil droplets are dispersed.

Either one or both of the colloid materials should be gellable and used in such concentration that the coacervate complex colloid material is gellable.

The droplets of oil in the capsules of the product are protected from contact with the surrounding environment by a thick self-supporting tough film of the colloid materials. The encapsulating complex colloid material may be hardened and water-insolubilized to a point where the capsules are highly resistant to heat and moisture. The encapsulating film of a capsule may contain one or more droplets of oil, the droplets in the latter case maintaining their identity by persistence of the emulsion interface film.

By "ionizable hydrophilic colloid material" are meant substances such as gelatin; albumen; alginates, such as sodium alginate; casein; agar-agar; starch; pectins; carboxy-methylcellulose; Irish moss; and gum arabic.

As has been said, in order that coacervation may occur, the two kinds of colloid ions, as they exist in the mixture before coacervation, must have different ionic charges. Some kinds of hydrophilic colloid ions in aqueous sols are negatively charged, regardless of the pH of the sol some kinds are positively charged, regardless of the pH of the sol; and some are amphoteric, having an isoelectric point above which they are negatively charged and below which they are positively charged. The electric charge characteristics of a hydrophilic colloid under consideration may be determined by

[Price 3s. 6d.]

POOR
QUALITY

Best Microscopic Copy

electro-phoresis in a manner to be described. In the event that one or both of the colloids used are amphoteric, the pH of the sols may be so adjusted that the colloid ions of the two kinds are of different electric charge. Amphoteric hydrophilic colloids of the same iso-electric point cannot be used.

In the process of coacervation, the complex colloid material deposits around the oil droplets to form the capsules.

In a further embodiment of the invention, the oil containing capsules are produced by a salt-coacervation process in which an emulsion is formed by mixing the oil and a single gellable hydrophilic colloid sol and causing coacervation of the colloid material by adding a salt solution to the emulsion so as to deposit the colloid material around droplets of the oil, the colloid material forming the capsules being subsequently gelled.

The microscopic capsules, made in an aqueous medium are several microns in diameter, and each contains one or more drops of oil surrounded by a relatively thick encapsulating wall of the gelled colloid material. If the capsules are dispersed in a great deal of water they may exist individually, but if the free water is removed the capsules tend to agglomerate like bunches of grapes until the mass becomes more or less solid.

By the process steps to be described, the colloid encapsulating material is rendered impermeable, as far as the oil is concerned, so that it cannot escape until the capsule is ruptured. In this way the oil is contained protected against environmental and other deleterious influences. In the event of the free water being removed, the capsules may be treated as solid material even though more than 50% of the weight of the mass may be oil in liquid form. If desired, the capsules may be hardened and rendered insoluble so that the free water may be driven off by heat, the dried material being immune to the destructive influence of water and other equivalent solvents.

The oils which may be used in the process are the water-immiscible oils which are inert as to the encapsulating material and which may be emulsified with an aqueous sol of the particular hydrophilic gellable colloid used. Among such oils are the mineral oils such as petroleum fractions; animal oils such as sperm oil; fish oils such as halibut liver oil; vegetable oils such as cotton seed oil, corn oil, castor oil, and coconut oil; essential oils from plants, and synthetic oils such as methyl salicylate and chlorinated diphenyl.

Among the gellable hydrophilic colloid

materials may be mentioned gelatin and agar-agar.

In the oil that is used to form the droplets which are surrounded by the encapsulating material, there may be dissolved various selected materials, or suspended solid material of colloidal size, such added substances, of course, being inert to the other ingredient materials. Among such finely divided solid substances may be mentioned dyes such as are used in making inks, solid chemical reactant substances which will be described, medicines, perfumes, and other materials which it is desired to have protected from the environment or which it is desired to have isolated for other reasons. Among substances which may be dissolved in the oil may be mentioned oil-soluble dyes, adhesives, and oil-soluble vitamins.

Among the most important uses for such material in an aqueous suspension is as a paper coating composition which forms a transfer film. The oil in the microscopic capsules so used would be of itself or contain a marking material which would be transferred to an underlying sheet by printing or marking pressures that rupture the capsules of the overlying film, to cause said marks on the underlying sheet. Transfer films of rupturable type which contain oily droplets of marking fluid are known, but such films are not composed of capsules. Such known transfer films consist of a continuous film phase of gelled hydrophilic colloid material having fluid droplets of oil dispersed therethrough. The aforesaid continuous film affords some opportunity for escape of the fluid droplets because of the sponge-like texture of the colloid gel film surrounding the voids which hold the oil. Cracks in the films will run right across the voids which hold the oil, releasing the oil. Such cracks may be caused by folding or rough handling of the material, or may be caused by unusual environmental conditions.

The product of this invention makes transfer films superior to those previously known, in that cracks in the film formed by the capsular material of this invention do not run across the capsules, but around them, so that the oil is not released by random cracks produced in the film. Moreover, the pore size of the complex colloid encapsulating film may be reduced during gelation and drying to render the encapsulating film impermeable to the oil inside, as will be explained.

Because all films of gelled hydrophilic colloid material are to a degree molecularly porous because of the nature of gel structures, the capsules will be more or less porous according to the control exer-

**POOR
QUALITY**

cised in forming them. If the gelation step is performed rapidly the pore size will be small and the capsules will retain by sieve action oils having relatively small molecules. If the gelation step is performed slowly the pore structure of the encapsulating material will be coarser. The hardening step is carried out in a high pH environment, as will be described, which makes the capsules harder, more heat resistant, and insoluble in water. If the capsules are used to hold marking fluids, small pores are desired, whereas if the capsules are to be used for other purposes where slow release of the oil from the capsules is desired, larger pores would be preferred. The process is flexible to achieve either condition.

Other uses for the capsules involve the protection of oils against the deteriorating influence of the environment, to confine the odours of oils such as perfume oils, and to prevent the reaction of oils with other substances during handling or storage. Further uses of such capsules are to confine medicinal oils to prevent them from being tasted upon being swallowed by a patient, to protect them from the deleterious influence of various environments in which they may be stored, or to protect such from contamination with substances with which they may be mixed.

If the capsules are to be dried, they may be dried in an oven and the resulting agglomerate material ground and washed to remove the oil which escaped during grinding, to form apparently dry granules or, if desired, the fluid suspended capsules may be spray dried in which event no comminution or washing is necessary. In the dry granular form the capsules containing the fluid oil are handled and stored in the same manner as other dry materials are handled and stored.

If desired, after gelation, any of the further steps of hardening the gelled material; separating the hardened gelled material from the remaining liquid; drying it; and comminuting it to the desired particle size, may be used.

The process steps, down to the gelation step, are carried out with the ingredients at a temperature above the gel point of the colloid material used, and gelation is brought about by cooling.

The finished product, before drying, may be used for coatings or films, as the capsules adhere together after drying, or the material may be cast into any wanted form.

If desired, after hardening and drying, the agglomerate mass of capsules may be comminuted to form fine granules of any desired size. The capsules, being so

small and tending in the agglomerate form to cleave between the capsules, are not destroyed to any great extent by comminution of the mass.

The invention will now be described with reference to the accompanying drawings, wherein:—

Fig. 1 is a ternary diagram showing the coacervation region of a sol of gelatin in water, using sodium sulphate as the salt.

Fig. 2 is a ternary diagram showing the coacervation region of a sol of gelatin in water using ammonium sulphate as the salt.

Fig. 3 is a ternary diagram showing the complex coacervation region of mixtures of gum arabic and gelatin aqueous sols without any artificial adjustment of the pH value, which is 4.5.

Fig. 4 shows an apparatus by which a colloid's ionic charge and iso-electric point may be determined.

The process of making the capsules by salt coacervation, in general, includes the first step of forming an emulsion of oil and a gellable colloid aqueous sol. This is made by dispersing the colloid in water, adding the oil and forming an emulsion by stirring. Next, after having determined the coacervate region of the sol, by making a diagram as shown in Figs. 1 and 2, as will be described, a coacervate is formed by the addition of a proper amount of an aqueous solution of a suitable salt. In order that the colloid will not gel prematurely the foregoing steps are performed at a temperature above the melting point of the colloid sol. Thereafter, the colloid is gelled by pouring the coacervate mixture into a cool solution of the same salt which was used for the coacervation, causing the colloid deposited around the individual oil droplets to gel. This gelled colloid capsular mass is washed with water and filtered to remove the salt. If it is desired to harden and insolubilize the capsular material, the filter cake is treated with a solution of formaldehyde. According to what use is to be made of the finished material, the free water is adjusted to the desired concentration, or the free water is removed entirely.

The preferred form of this embodiment of the invention utilizes gelatin, preferably high quality pig-skin gelatin which has an iso-electric point of pH 8. Inasmuch as the finished encapsulated material will find an important use in the making of coating compositions which will form a transfer film on record material, such as paper, the preferred oil used is trichlorodiphenyl which is relatively non-volatile, inert, and which can

be obtained in a colourless and pure form. Into this trichlorodiphenyl may be dissolved a colourless colour-reactant such as crystal violet lactone, which is 3,3 bis
 5 (*p*-dimethylaminophenyl)-6-dimethyl-amino phthalide. The phthalide compound has a white crystalline structure and, when dissolved to the extent of about 3%, by weight, in the trichlorodiphenyl
 10 and placed in contact with a sheet of paper sensitized with attapulgate, will turn to a dark blue colour similar to crystal violet. When fluid dispersed capsular material containing this oil is applied
 15 to a sheet and dried to form a transfer film, the capsules may be ruptured locally at points of printing and marking pressures to release the oil which will thereupon come in contact with the sensitized undersheet. In making up the preferred
 20 material, one gallon of an oil-in-water emulsion of 20 parts, by weight, of trichlorodiphenyl containing the crystal violet lactone and 100 parts, by weight, of a sol of 10%, by weight, of pigskin
 25 gelatin in water, is prepared, the emulsifying continuing until the drop size of the oil is from 2 to 5 microns. This material is kept at 50° Centigrade to prevent the gelatin from gelling. With the
 30 temperature of the ingredients still kept at 50°, coacervation is induced by adding, slowly and uniformly, four-tenths of a gallon of 20%, by weight, of sodium sulphate in water. The uniform addition
 35 of this material is accomplished by continuous agitation. To gel the coacervate, the heated coacervate mixture is poured into 10 gal-
 40 lons of 7%, by weight, of sodium sulphate in water at 19° Centigrade, with agitation. At this point the encapsulation of the oil with gelled hydrophilic material has taken place and the further steps are
 45 to put it in condition for use as is intended. The material is filtered and washed with water, the temperature being kept below the melting point of the gelatin, to remove the salt. If desired,
 50 the filtered material is hardened by combining it with 2 gallons of a 37% solution of formaldehyde in water. This hardened mass then is filtered and washed to remove the residual formaldehyde. The result-
 55 ing filter cake is adjusted to the proper water content by the addition of water or the removal thereof, by ordinary means such as centrifuging or spray drying, and the material is ready for use. If this
 60 material is intended for a paper coating composition it is kept in aqueous suspension and applied directly to the paper which is then dried leaving the capsules adherent to the paper and to each other in
 65 a film.

In determining under what conditions with particular materials coacervation takes place, resort may be had to the formation of a ternary diagram resulting from a testing of various amounts of pig-
 70 skin gelatin and sodium sulphate solution, whereas Fig. 2 shows the results of testing various amounts of the same gelatin with an ammonium sulphate solution. In the causation of coacervation by use of
 75 a salt, the salt attracts water away from the colloid material causing the colloid material to separate, forming, in the vessel in which this step is taken, after they
 80 are allowed to separate by gravity, a colloid-rich fluid in the bottom and a layer extremely poor in colloid material on top. The tests which are made to determine the coacervate region as far as amounts of
 85 material are concerned can be done with the colloid sol and the salt solution without the oil. Inasmuch as it is impractical to work with solutions of gelatin in
 90 which there is less than 80% water, because of viscosity, the diagrams of Figs. 1 and 2 deal in that portion of the ternary scale above 80% water. The line 20 in Fig. 1 and the line 21 in Fig. 2 represent
 95 80% water, the horizontal lines being indexed with the intermediate percentages of water. Coacervation is noticed by a clouding effect appearing in the sol which transmits less light than normal. This
 100 may be noted by passing a beam of light through the sol as the salt solution is added and estimating by eye the change towards a cloudiness, or an electric photo-
 105 meter may be used. A particular sol is made of the pigskin gelatin and various solutions of sodium sulphate in water are added thereto. Referring to Fig. 1, with
 110 a starting point of any place on line 23, that is to say any sol of gelatin and water having less than 20% gelatin content, by weight, the aqueous sodium sulphate solu-
 115 tion is added. For instance, if a 10% gelatin in water sol is used, the starting point would be 24 (Fig. 1) on line 23. If now a 15% solution of sodium sulphate in water, as would be plotted at point 25,
 120 is added slowly which would be plotted along the dotted line 26, at point 27 a clouding effect will be noticed which means that the gelatin in water sol is changing so that the entire mass of gela-
 125 tin in a liquid phase is contracted because of the increased interaction between the gelatin molecules. This clouding effect, first noticed at point 27, will continue as more of the sodium sulphate solution is
 130 added. During the experiments to determine the coacervate line 28 by various experiments with different concentrations of sol and salt solution, the ingredients are kept at about 50° Centigrade. As

another example in determining the line 28 of Fig. 1, a 17½% sol of gelatin in water, represented by point 29, is treated with a 12½% solution of sodium sulphate in water as represented by point 30. As this sodium sulphate solution is added to the aqueous gelatin sol, the addition takes the mixture along the line 31 toward point 30, the clouding effect of coacervation becoming apparent at point 32. By making a number of such experimental additions of the sodium sulphate solution to various sol concentrations, the contour of line 28 may be ascertained and the ranges within which coacervation by the addition of sodium sulphate solution to the gelatin sol may be ascertained. The region to the right of line 28 is the coacervate region of the mixture but the addition of salt solution should not be carried far past the line 28 in actual practice, the more salt solution added the more aggregation occurring until a lumpy mass is formed. In a similar manner the line 33 of Fig. 2 may be determined by the use of ammonium sulphate solution.

It will be evident that the ammonium sulphate solution is not as efficient in action as the sodium sulphate solution and the same differences occur with other salts. Useful salts for coacervation may be made from the cations $\text{Na} > \text{K} > \text{Rd} > \text{Cs} > \text{NH}_4 > \text{Li}$ and the anions $\text{SO}_4 > \text{Citrate} > \text{Tartrate} > \text{Acetate} > \text{Cl}$, such being arranged in the order of their effectiveness in this process.

When oil droplets are present the gelatin still in the liquid phase starts to draw together entrapping the oil droplets by deposition of the sol material around them individually, forming a strong wall, and upon gelation of the colloid material the capsules are complete.

Reference has been made to the fact that the size of the pores in the encapsulated material may be controlled during the gelling process. The faster the gelation of the colloid the finer the pore size of the gelled structure will be, and *vice versa*. As mentioned hereinbefore, the gelation of the gelatin was accomplished by pouring the coacervated mixture, amounting to about a gallon and a half, into 10 gallons of relatively cool water at about 19° Centigrade. This causes rapid cooling and rapid gelation of the gelatin, resulting in a pore size so small that the encapsulated trichlorodiphenyl cannot escape through the capsule walls. Less rapid cooling will result in pores of larger size and the oil used may gradually escape or not as is determined by the size of the pores in the encapsulating film and the size of the oil molecules.

The method of making the capsules

from complex hydrophilic colloid material in general, includes the steps of forming a first sol by dispersing one of the selected colloid materials in water; introducing the selected oil and forming an oil-in-water emulsion by beating or stirring; forming a second sol, similar to the first in concentration and amount, of the other selected colloid material and water; mixing the emulsion and the second sol; adjusting the pH of the mixture, if necessary, so that the ions of the two colloids have different electric charge; diluting with water, and/or changing the pH of the mixture until the complex coacervation takes place, all of the foregoing steps having been performed at a temperature above the gelation point of the colloids; cooling the resulting complex coacervate material to cause it to gel, as by subjecting it to an environment having a temperature below the gelation point of the coacervated complex; if desired, adjusting the pH of the material toward the alkaline side to promote hardening of the encapsulating material; treating the gelled material with a solution of formaldehyde, or equivalent, in water to harden the encapsulating material; and finally, if desired, separating the capsules from the remaining liquid, drying them, and comminuting them if aggregated.

The gum arabic and gelatin, preferably, are used in the same concentration and amount to form the mixture. The amount of colloid used up as the emulsifier is so small as to be disregarded in computing the amounts of the colloid ingredients to be used in the mixture to be coacervated.

The iso-electric point of an amphoteric hydrophilic colloid may be determined by forming an aqueous sol of it and testing it in the apparatus of Fig. 4 to determine the charge of the colloid ions. The thistle tube is filled with the sol 22, with the stop cock 21 closed. Water buffered to the pH of the sol is then introduced into the U-shaped portion 20 and the stop cock opened to admit the sol slowly until boundary layers are formed in both legs. Direct current is applied to the electrodes 23 and 24. If the colloid ions have negative charges, the separating interface line between the water and the sol will be higher in the leg containing the positive electrode than in the arm containing the negative electrode, as shown at 25, and *vice versa*. The iso-electric point may be ascertained by repeating the experiment with sols of various pH value until the boundaries remain level when electric potential is applied. Similarly, the natural charge of an ionized non-

amphoteric hydrophilic colloid may be ascertained.

It is also necessary, in carrying out the process, to determine, by experiment, the dilution conditions under which the two selected kinds of colloids coacervate to form a colloid complex, and this may be done by testing sols containing the selected two colloids in various concentrations. This may be done experimentally for various pairs of colloids by preparing sols of them in various concentrations, mixing them, and diluting them slowly with water until a cloudy appearance indicates that complex coacervation has taken place. On standing, two layers will form, the coacervate colloid-rich layer still being liquid. Fig. 3 is a ternary diagram, the shaded area 30¹ at the top showing the region in which various concentrations of gum arabic and gelatin, having an iso-electric point of pH 8, coacervate. Such a diagram may be made for any two colloids with which it is desired to form the complex coacervate. Two sols are formed that are compatible. If the concentration of colloid material is too great, as in the region under curve 31¹, the sols will be incompatible and form two phases. The diagram is made by testing the mixtures of sols without the oil, as the oil will make the mixture opaque, so that the cloud point, indicating incompatibility or coacervation, cannot be seen.

If the mixture of colloids cannot be made to form a complex coacervate, the pH may be adjusted up or down to a point where experiments show that coacervation does take place upon dilution. Temperature also may be varied to a point where experiments show that coacervation takes place.

Considering the diagram of Fig. 3 more specifically, concentrations of the particular colloids below line 31¹ form incompatible mixtures; that is, the compatible sol mixture separates into two sols. As an instance of this two sols are made, the first with 30 parts of gum arabic and 65 parts of water, and the second with 40 parts gelatin and 65 parts water. The light transmission of each sol is noted. If, now, these two sols are mixed together, the light transmission of the mixture is less than that of either sol alone, and, eventually, two layers will be formed, one being rich in one colloid and the other rich in the other colloid, showing the incompatibility of the sols and the unsuitability of the mixture for complex coacervation. The unsuitable mixture discussed is plotted at 32². The light transmission may be roughly gauged by eye but is more accurately determined by an electrophotometer. Now, if two sols were

made with the same gum arabic and gelatin, the first with 10 parts gum arabic and 90 parts water, and the second with 10 parts gelatin and 90 parts water, and mixed, the same clouding effect is noticed. In this case, however, a complex colloid is formed, by coacervation, forthwith and will separate out from the water by gravity, in time. In this case, the upper layer has practically no colloid material in it and will transmit light freely, whereas the lower layer is very cloudy. It is to be understood that there is no oil present in these tests.

A number of mixtures of low-concentration sols tested in the above manner will determine region 30¹, which is the coacervate region. Although the boundary of region 30¹ is given a sharp line, said boundary is not sharp, due to molecular weight variation in the particular polymers involved. However, it is readily ascertainable when the complete coacervation region has been entered. The region under line 31¹ and the enclosed regions 30¹ having been determined, a point such as 33¹ is picked for making the mixture of sols for use in the process of this invention. Point 33¹ represents a sol mixture of 10% gelatin, 10% gum arabic, and 80% water. Dilution of this mixture with water added slowly produces the coacervation, the dotted line 34 representing the dilution necessary to take the mixture into the centre of the coacervation-region.

A ternary phase diagram, prepared as described, will furnish the necessary information for carrying out the process of this invention with any two selected colloid materials having the necessary characteristics of different ionic charge and gellability.

First, a specific example of the process will be given, when dilution only is used. A sol is made of 20 grams of gum arabic dissolved in 160 grams of water. Gum arabic in water always forms negative ions regardless of the pH. Into this is emulsified 80 grams of trichlorodiphenyl. A second sol of 20 grams of pigskin gelatin, having an iso-electric point of pH 8, and 160 grams of water is prepared, and this second sol is mixed with the emulsion. A volume of water then is added slowly to the mixture drop by drop, or by spray, with constant stirring until coacervation starts and is continued until the particle size of the oil droplets on which the coacervate material is deposited is as large as desired, the less water used the smaller the particle size. All of the foregoing steps are carried out with the ingredients at 50° Centigrade. The resulting coacervate mixture is poured into water at 0° Centigrade, enough water being used to

bring the total weight of ingredients to 3960 grams. The mixture is agitated and thereafter is allowed to stand for an hour at not over 25° Centigrade. The formation of the capsules is now completed, and they may be used in suspension as a coating for surfaces or for other use as a fluid, or they may be dried and comminuted.

The capsular suspension resulting from the step of gelation contains the coacervate capsule in usable form, the optional hardening step described above being used where it is desired to use heat to drive off the water or to render the capsules insoluble. If it is desired to use the capsules as a coating material for paper, the encapsulated particles may be concentrated and applied to the paper and air-dried at a temperature below the melting point of the gel complex. Most of the water can be removed by centrifuging or filtering.

However, fast drying is desirable in coating paper, and the hardening step is provided as an optional step to permit the water to be driven off by heat.

The optional step to obtain a hardened capsular product from the coacervate suspensions requires the preferable step of adjusting the pH of the suspension of capsular material to between 9 and 11, by use of sodium hydroxide, and cooling the resulting slurry to 0 degrees to 5 degrees Centigrade; pouring in 19.8 grams of 37% by weight formaldehyde in water adjusted to pH 9—11 with sodium hydroxide and agitating for at least 10 minutes; and separating the resulting hardened capsules from the remaining liquid by filtering or centrifuging. Finally, if desired, the mass may be dried with heat (the hardening step preventing melting of the encapsulating material) and comminuted to the required granular size.

In filtering first the free water is removed on a suction filter, then the filtrate mass is heated up to a maximum of 85 degrees Centigrade to drive out the water which is bound in the gel network of the capsules. The water driven out of the gel, yet present in the mass, results in the formation of a smooth slurry of the capsules, which may itself be used while hot, or filtered again. The hardened capsules suspended in water may be spray-dried in a hot environment to remove both the free water and the gel-bound water, or the spraying may be done after a first filtering step to remove the free water. If the slurry is allowed to cool after the first filtering and subsequent heating to drive out the water from the gel network, the water of the slurry will return to the gel network, leaving the mass as it was before heating. To avoid this return of the water to the

capsule gel material, a dry hydrophilic colloid which preferentially will bind most of the water to itself is added to the hot slurry. With the materials used in the coacervate complex, high-viscosity polyvinyl alcohol added in the dry form will do, enough being used to attain the desired viscosity of the cooled material. The sol formed of the driven-off water and the added polyvinyl alcohol, or equivalent, will keep the material in fluid form on cooling.

The amount of oil used in proportion to the colloid ingredients of the complex may be varied greatly and any amount up to 100 grams or more of the trichlorodiphenyl may be used with 40 grams of colloid material. Generally speaking, the more oil used, the thinner the encapsulating sheath will be the oil drop size being maintained the same.

If the oil and the colloid material were used in equal amounts by weight, the capsule skin thickness would be greater. In addition to such thickening of the skin, aggregates of capsules are formed which seem to be encased in a mass of the colloid complex, whereas with the thinner-skinned capsules they agglomerate in bunches like grapes. Ordinarily, the aggregations and bunchings of the capsules are on a microscopic scale, but large enough aggregates to be barely visible to the unaided eye may be formed if sufficient dilution with water occurs in the coacervation step.

As examples of synthetic oils, mineral oils, vegetable oils, and animal oils which may be used in place of the trichlorodiphenyl used in the preferred embodiment of the invention may be mentioned methyl salicylate, petroleum oil, coconut oil, castor oil, and sperm oil. These oils were used in a proportion of 1 to 1, by weight, with the colloid materials. The hardening step when methyl salicylate is used must be at about pH 7, as at a pH above 7 there is chemical reaction between the sodium hydroxide and the methyl salicylate through the pore openings in the capsules. Whenever any such reaction is likely to occur between any of the ingredients, similar precautions should be taken.

The mixture of emulsion and sol need not contain equal parts, by weight, of the two colloids used, as will be evident from the diagram of Fig. 3. For instance, if the mixture contained 5% gelatin, 15% gum arabic, and 80% water, the dilution starting point would be at 38 on the diagram, and the coacervation region could be obtained by diluting the mixture with water, in which event line 39 is followed. In this proportion of colloid material and water, the dilution could be

made with a dilute gelatin sol. If a 5% gelatin sol were used, as the diluent the line of dilution would be represented by broken line 40. If the starting mixture is at point 41, dilution with water would be along line 42, and dilution with a 5% gum arabic sol would be along line 43. From an observation of the diagram of Fig. 3, it will be obvious that less water dilution is needed when moving along centre line 34 than when entering region 30¹ obliquely. The examples of starting mixtures represented at points 33¹, 38, and 41, are representative only and should not be deemed the only starting mixtures that could be used, as any convenient point between line 31¹ and region 30¹ could be a starting point.

Generally speaking there should be no chemical reaction between the oil and the colloids, and the materials should be chosen with that point in mind.

Other agents than sodium hydroxide for adjusting the pH of the coacervate mixture are sodium carbonate and potassium hydroxide.

As was mentioned earlier, the encapsulated material could be either a printing fluid of an intrinsic colour or a reactive ink that changes to a distinctive colour when applied to sensitized record material. As examples of an oil with a colour added may be mentioned Sudan III or Sudan IV dye in the before-mentioned trichlorodiphenyl. As examples of an oil with a colourless colour reactant added may be mentioned 3,3 bis(*p*-dimethyl-amino-phenyl)-6-dimethylamino phthalide, or 3,3 bis(*p*-dimethylamino) phthalide in the trichlorodiphenyl.

A process will now be described where the mixture of sols and dispersed oil has the pH raised, before water is added, to a point where coacervation by dilution will not occur, and, after the addition of water, it is returned to the coacervate region by pH change.

20 grams of gum arabic is dissolved in 160 grams of water and emulsified with 80 grams of trichlorodiphenyl. This emulsion is mixed with a sol made of 20 grams of pigskin gelatin, with an iso-electric point of pH 8, and 160 grams of water. If desired, the emulsion may be made with the gelatin sol instead of the gum arabic sol, the sol which is used for making the emulsion being a matter of choice, or the sols may be mixed and the oil emulsified with the mixture. Good results may be obtained using up to 100 grams, or more, of the trichlorodiphenyl. The pH of the mixture of colloids and oil is about 4.5, and a complex coacervate will form if diluted according to the ternary diagram of Fig. 3. The process of dilution, when

used, must be slow and uniform to ensure proper deposition of the colloid material around the oil drops. To prevent this tedious dilution, the pH is adjusted to 5 or higher with 20% sodium hydroxide in water. The pH condition makes it impossible to cause complex coacervation of the colloids by the addition of the amount of water to be used. Next, 500 grams of water is introduced into the mixture, and the pH is slowly adjusted back to 4.5, which is in the complex coacervate range. 10% acetic acid in water may be used for this pH adjustment. The 500 grams of water is a variable item, and, therefore, a larger or smaller amount may be used, depending on the oil drop size and the final aggregate size that is desired. In general, the larger the oil drop size the more water is needed, and the less water used the smaller will be the size of the capsule aggregates.

In all the foregoing steps, the ingredients are kept at 50 degrees Centigrade, and the mixture is being continuously agitated, but not so as to cause foaming. By adjusting the pH back to 4.5, the mixture is taken into the complex coacervate region, and the complex colloid is deposited around the oil droplets. To harden the capsules—that is to say, to harden the encapsulating material—3½ grams of 37% formaldehyde in water is added to the mixture with agitation. This last step of adding the formaldehyde is also done with the ingredients kept at 50 degrees Centigrade. In order to complete the hardening action, a subsequent pH adjustment after gelation is necessary to bring the mixture to the alkaline side.

The mixture is next gelled by lowering the temperature to 10 degrees Centigrade during a 30 minute interval, with agitation, whereupon the complex encapsulating material forms a gel within which the oil droplets remain fluid. After this, the pH is adjusted to 9 with a 20% solution of sodium hydroxide in water. Sodium carbonate may be substituted for the sodium hydroxide, if desired.

This last form of bringing about complex coacervation is generally more efficient than that where large quantities of water are used to dilute the mixture, in accordance with the ternary diagram of Fig. 3. In this modified form of the process, wherein the complex coacervation is brought about by adjusting the pH, a more efficient use of the colloid material is made—that is to say, practically all of the colloid material goes into the making of the capsule walls—whereas, in the dilution form of causing complex coacervation, some of the complex colloid material exists apart from the oil droplets.

The capsular material, containing the oil droplets, made in accordance with the last mentioned process, is of such consistency that it may be used directly to coat on paper to form a film in which each of the oil droplets is enclosed in its own hardened colloid capsule. This material may also be dried and comminuted, as was the case with the material made by the dilution form of the process. In fact, the material is practically the equivalent of that made by the dilution form of the invention except for the improvement noticed in the efficient utilization of the colloid material, and except for the fact that not so much water needs to be removed.

That the capsules actually retain the oil droplets has been proved in various ways. The dried capsular material was placed in a Soxhlet extractor with toluene and subjected to extraction for a week. The material was then removed and dried. Upon crushing the capsular material, oil was released. Paper upon which a film of the material containing 3,3 bis(*p*-dimethylaminophenyl)-6-dimethylamino phthalid in the oil droplets was similarly treated in the Soxhlet extractor. Upon removal and drying it was used as a transfer sheet and placed over paper coated with attapul-gite clay. It made marks on the clay-coated sheet when subjected to printing and writing pressures, that were as intense as marks made therewith before the extraction attempt. The same paper was put in an oven and kept there with an amount of unprotected oil equal to that in the paper. Whereas the unprotected oil evaporated in one day, there was no evidence of any loss of oil from the paper even though let in the oven for ninety days at the same temperature.

What we claim is:—

1. A microscopic oil-containing capsule, wherein the casing thereof includes a gelled hydrophilic colloid material formed around droplets of the oil by coacervation.

2. A method of forming microscopic oil-containing capsules, wherein two substances, at least one of which is a gellable hydrophilic colloid material and capable of producing coacervates when mixed with the other substance, are brought into contact in the presence of an emulsion formed from the oil and at least one of the substances, such that when the coacervation occurs, the gellable hydrophilic colloid material is formed around droplets of the oil to produce capsules and thereafter gelled.

3. A microscopic oil-containing capsule, as claimed in Claim 1, wherein the oil droplets are enclosed by a single gel-

lable hydrophilic colloid material formed around the oil droplets by salt-coacervation.

4. A microscopic oil-containing capsule as claimed in Claim 1, wherein the oil droplets are enclosed by a gelled complex hydrophilic colloid material formed by coacervation of two hydrophilic colloid substances.

5. A method of forming microscopic oil-containing capsules as claimed in Claim 2, including producing an emulsion by mixing the oil and a hydrophilic colloid solution, causing coacervation of the colloid material by adding a salt solution to the emulsion so as to deposit the colloid material around droplets of the oil and subsequently gelling the colloid material formed around the oil droplets.

6. A method of producing microscopic oil-containing capsules as claimed in Claim 2, wherein a mixture is formed of aqueous solutions of two hydrophilic colloid substances in which the oil is emulsified, each colloid having different ionic charges in the mixture and at least one of the colloids being gellable, causing coacervation of the colloid material whereby it deposits around the oil droplets as a complex colloid and subsequently gelling the complex colloid material.

7. A method of producing microscopic oil-containing capsules as claimed in Claim 5, wherein an emulsion is formed from an aqueous solution of gelatin and oil at a temperature sufficiently high to prevent the gelatin from gelling, thereafter adding a salt solution at the same temperature to effect coacervation and cause the gelatin to deposit around droplets of the oil and subsequently immersing the coacervates in a further quantity of the salt solution having a temperature sufficiently low to gel the gelatin.

8. A method as claimed in Claims 5 or 7, wherein the salt solution is either sodium or ammonium sulphate in water.

9. A method as claimed in Claim 7, wherein cooling of the coacervates is performed rapidly in order to obtain rapid gelation of the gelatin so as to reduce the pore size to a minimum.

10. A method of making microscopic oil-containing capsules of gelled complex hydrophilic colloid material as claimed in Claim 6, including forming an oil-in-water emulsion with an aqueous solution of a first ionizable hydrophilic colloid material as the external phase and a selected oil as the internal phase, mixing the emulsion with an aqueous solution of a second hydrophilic colloid material, said colloid materials being used in such concentration that they are compatible in the mixture and such that the complex

to be made therefrom is gellable after coacervation, causing coacervation of the colloid materials at a temperature above the gel point of the colloid material and subsequently cooling the coacervate mixture to cause gelation of the complex colloidal mixture forming the capsules.

11. A method as claimed in Claim 10, wherein the mixture is diluted uniformly with water in sufficient quantity to cause complex coacervation of the colloid materials.

12. A method as claimed in Claim 10, wherein the pH value of the mixture is adjusted to a higher value so that complex coacervation will not be brought about by water-dilution of the mixture, adding water in an amount which would have caused complex coacervation had not the pH value been adjusted to the higher value, adjusting the pH value to its original figure so as to effect the deposition of a complex coacervate material about the oil droplets.

13. A method of making microscopic oil-containing capsules of complex colloid material as claimed in any of Claims 2, 6, or 10, comprising making an aqueous solution of gum arabic, making an aqueous solution of gelatin having an iso-electric point of pH 8, dispersing in either a water immiscible oil, mixing the resulting emulsion and the other solution together and causing the colloids to form a complex coacervate which entraps the

oil droplets to form a plurality of microscopic capsules and thereafter lowering the temperature of the coacervates until the complex colloid material gells.

14. A method of making microscopic oil-containing capsules claimed in any preceding claim, wherein the oil is colourless and has dissolved therein a colourless colour reactant substance possessing adsorption characteristics.

15. A method of forming microscopic oil-containing capsules claimed in any preceding claim, wherein the gelled hydrophilic colloid material is hardened after coacervation by treatment with formaldehyde.

16. A method of forming microscopic oil-containing capsules as claimed in Claims 2, 6, 10, or 13, wherein, after gelation, the pH value of the suspension of capsular material is adjusted by the use of sodium hydroxide, cooling the resulting mixture and adding an aqueous solution of formaldehyde having a pH value adjusted to the adjusted pH value of the suspension so as to produce a hardening of the oil containing capsules.

17. A method of producing microscopic oil-containing capsules by coacervation, substantially as described and in accordance with data contained in the ternary diagrams shown in Figs. 1, 2, and 3, of the accompanying drawings.

E. T. BEAVIS,

Agent for the Applicants.

FIG. 1

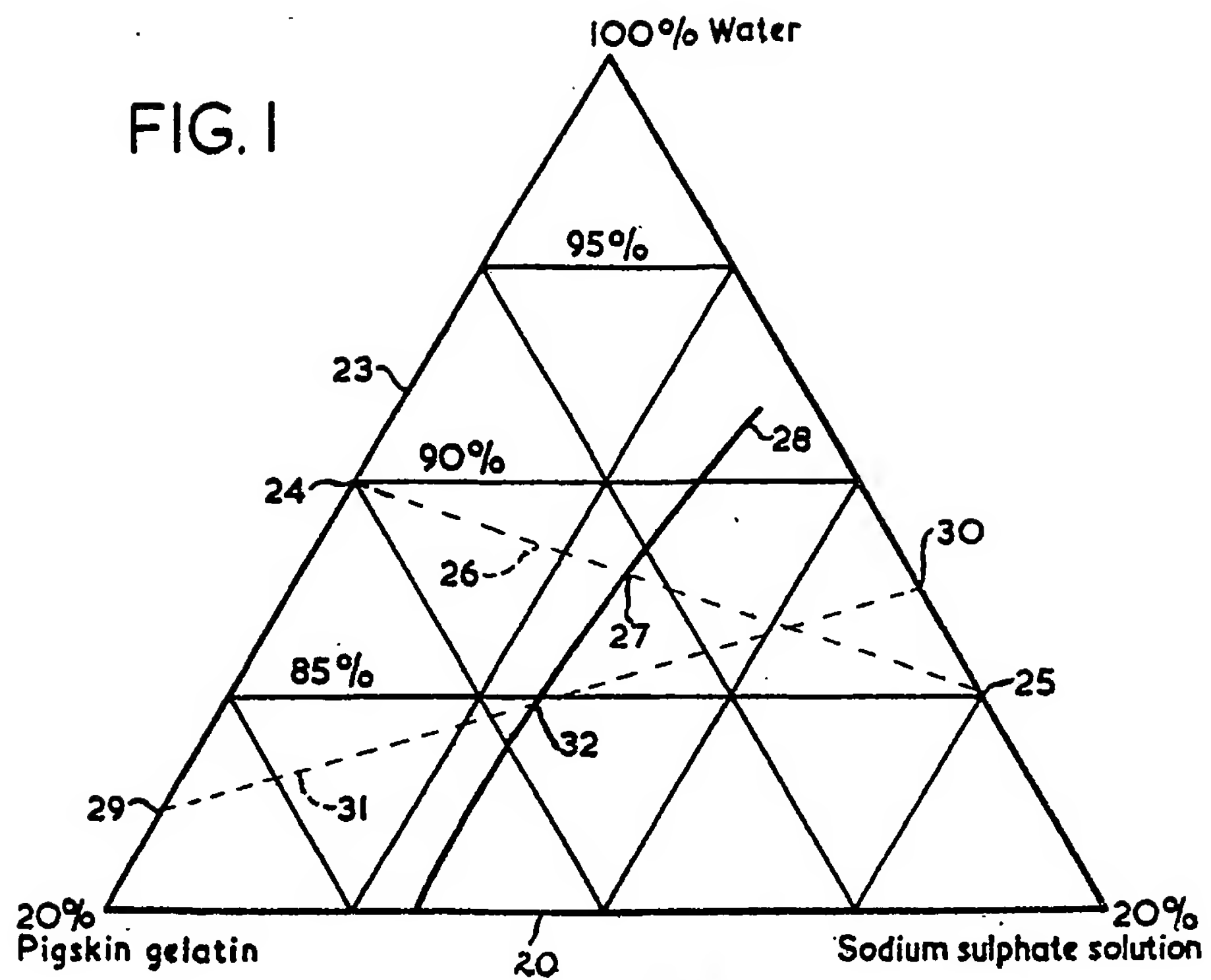


FIG. 2

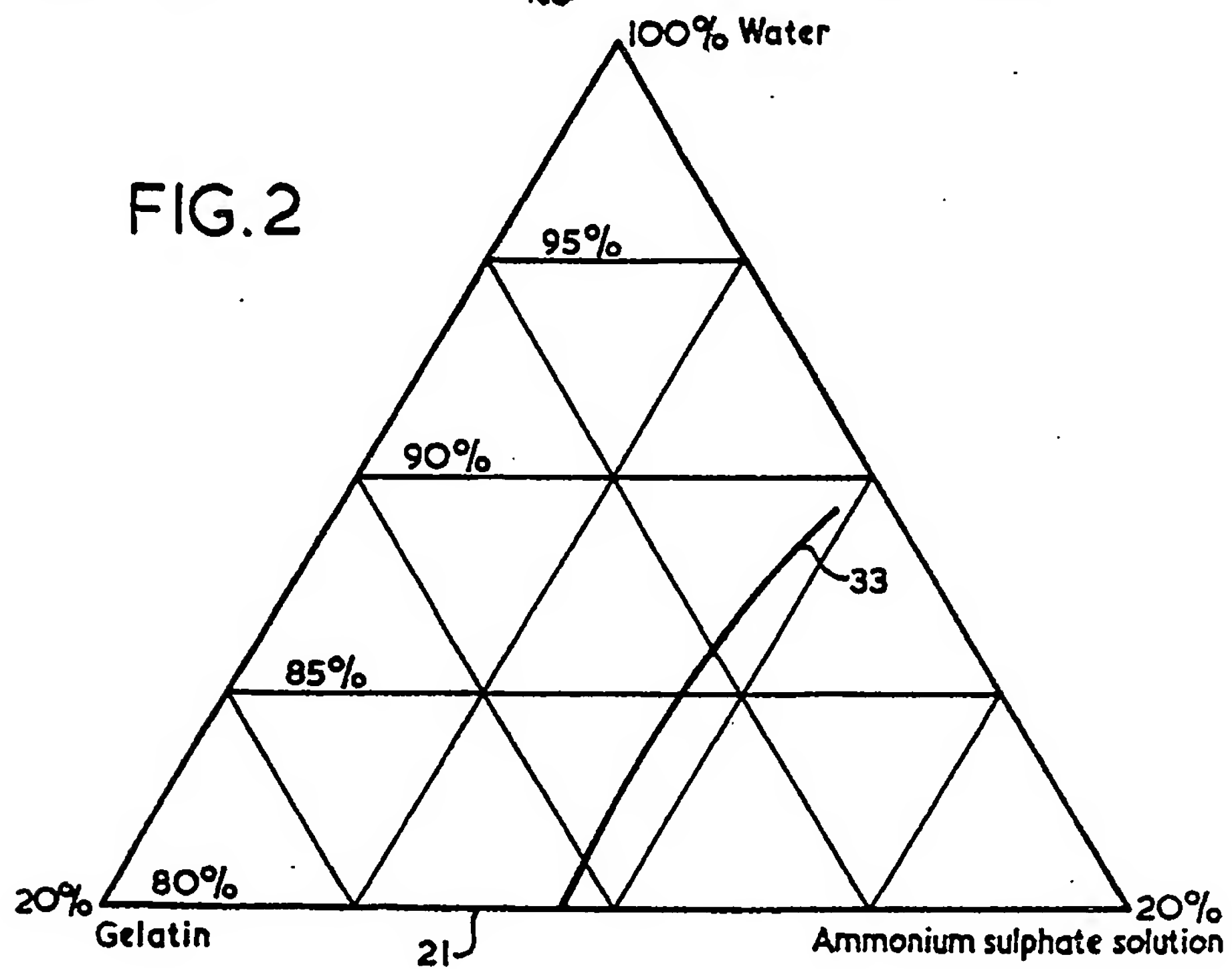
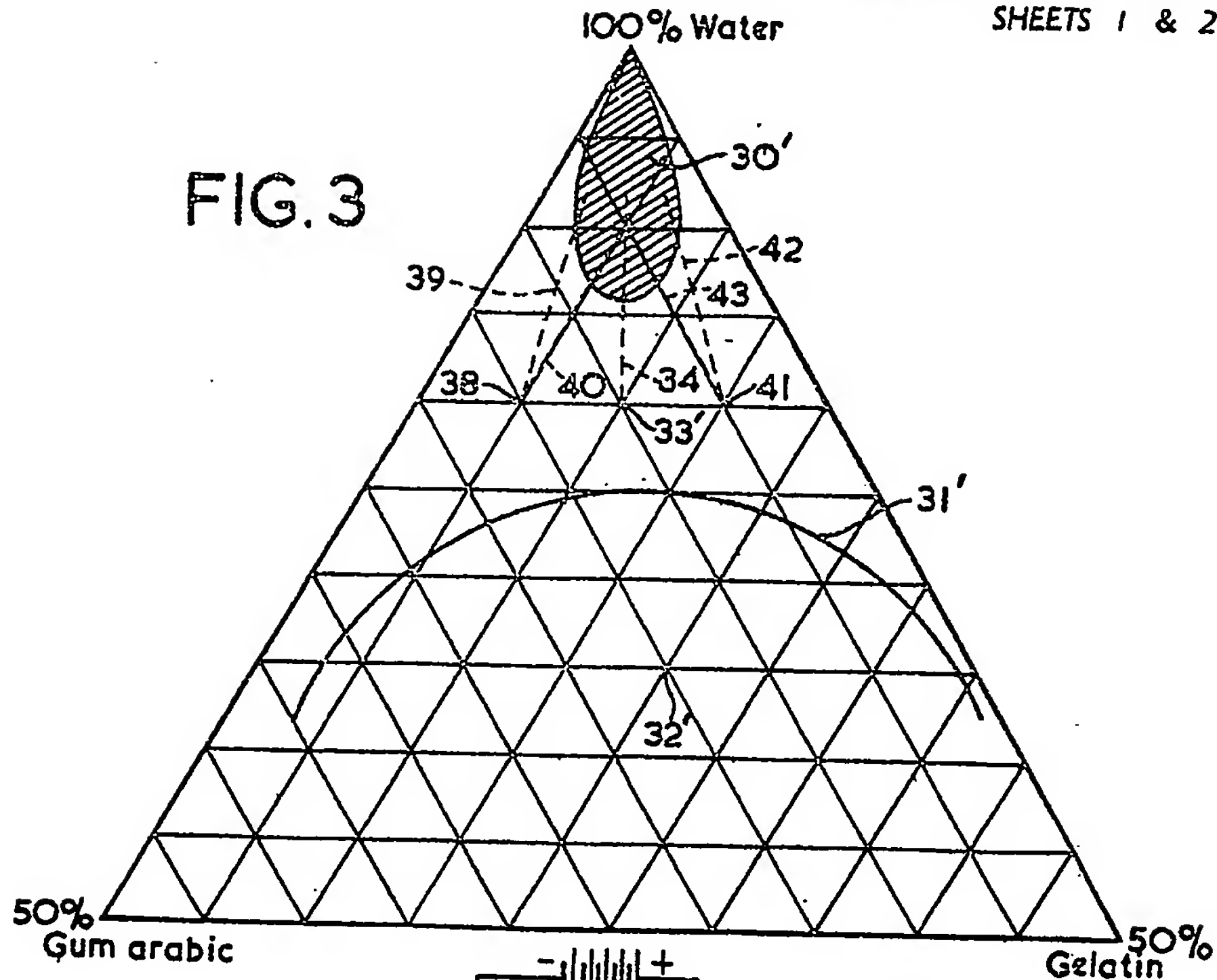
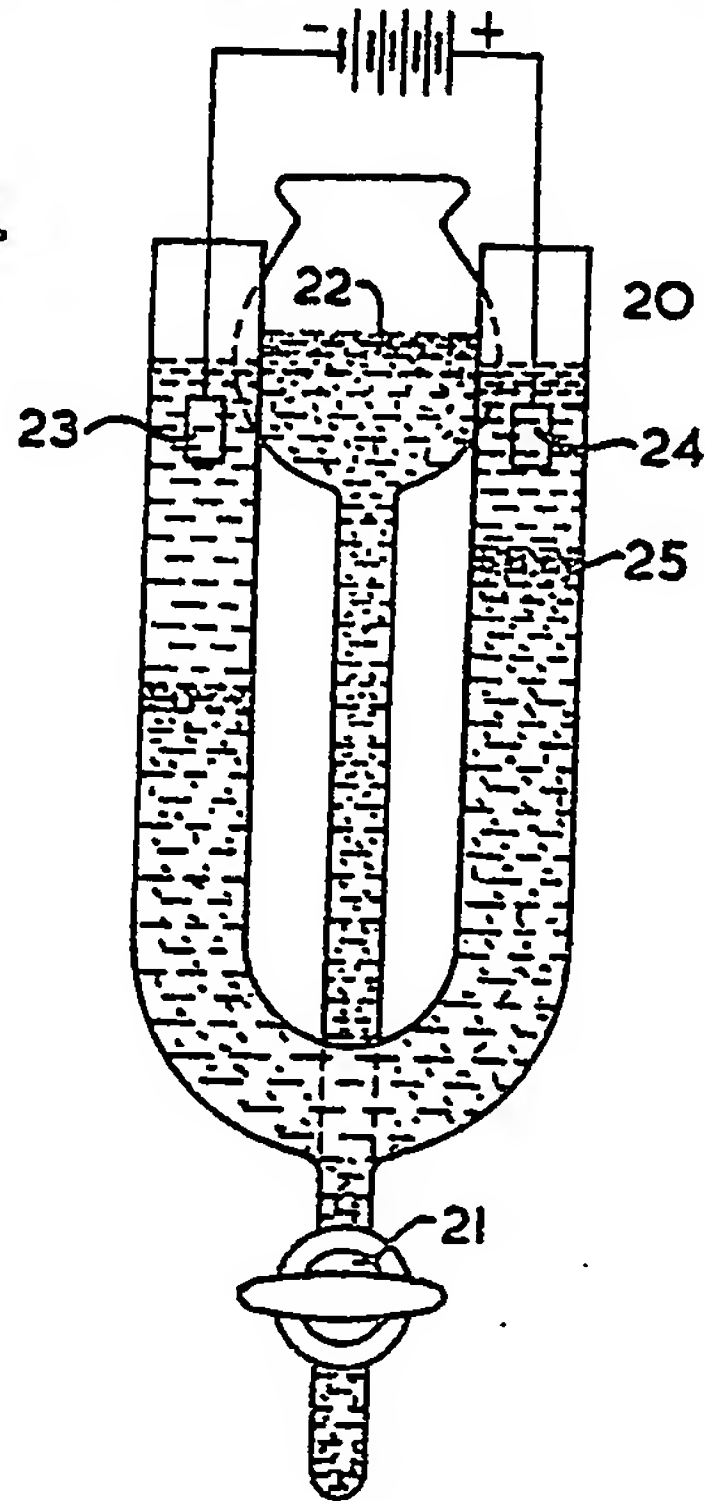


FIG. 3

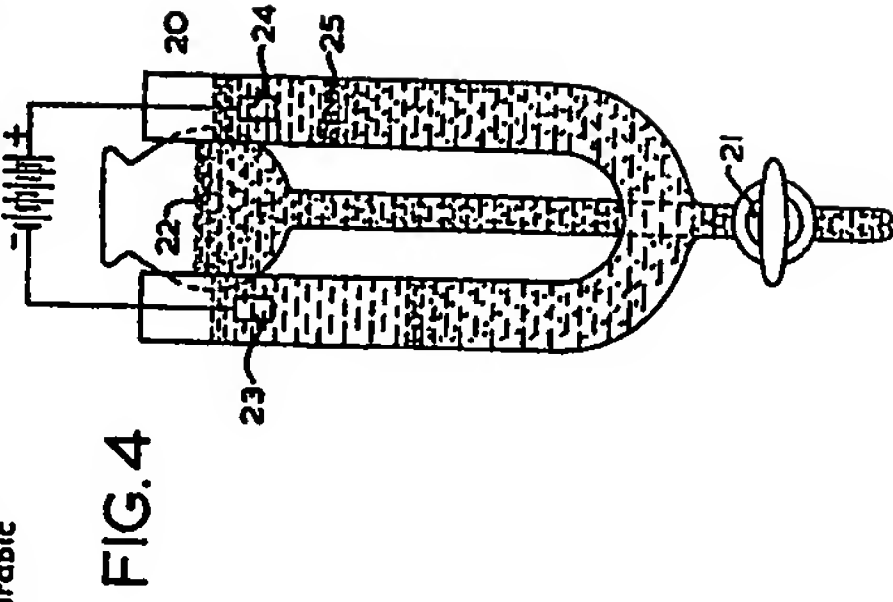
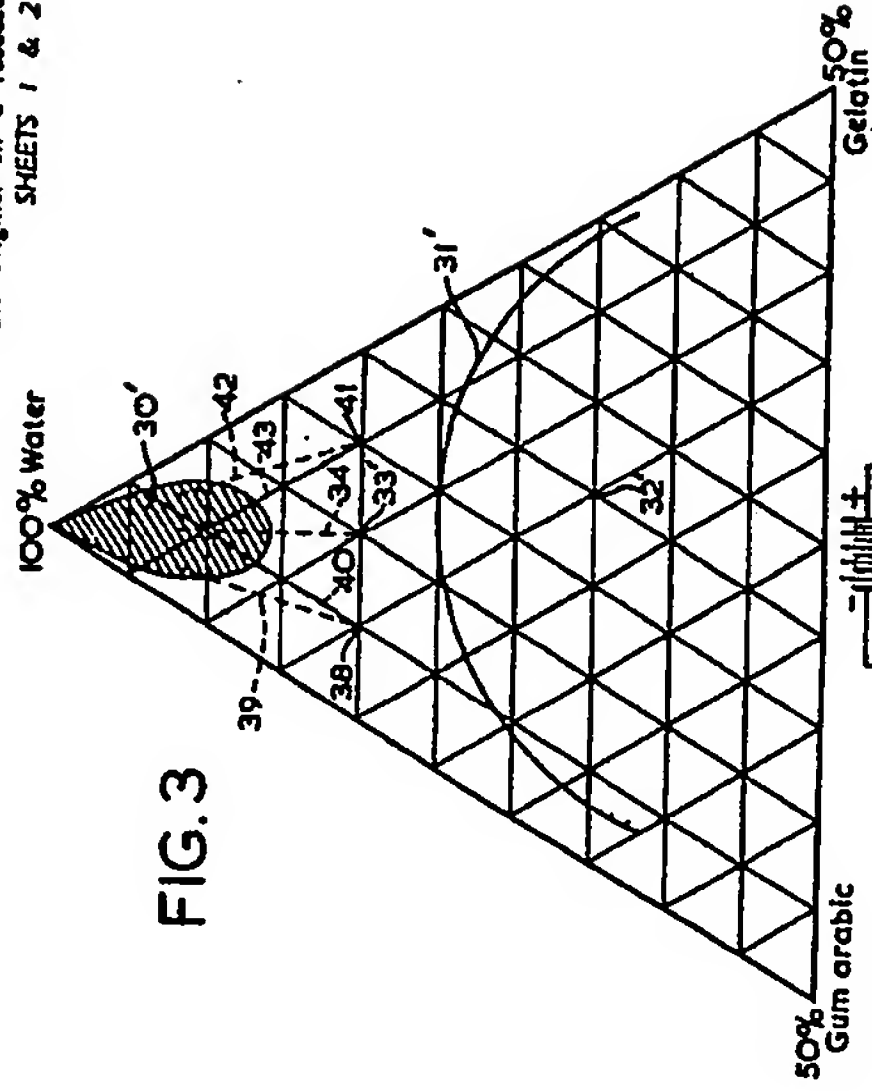
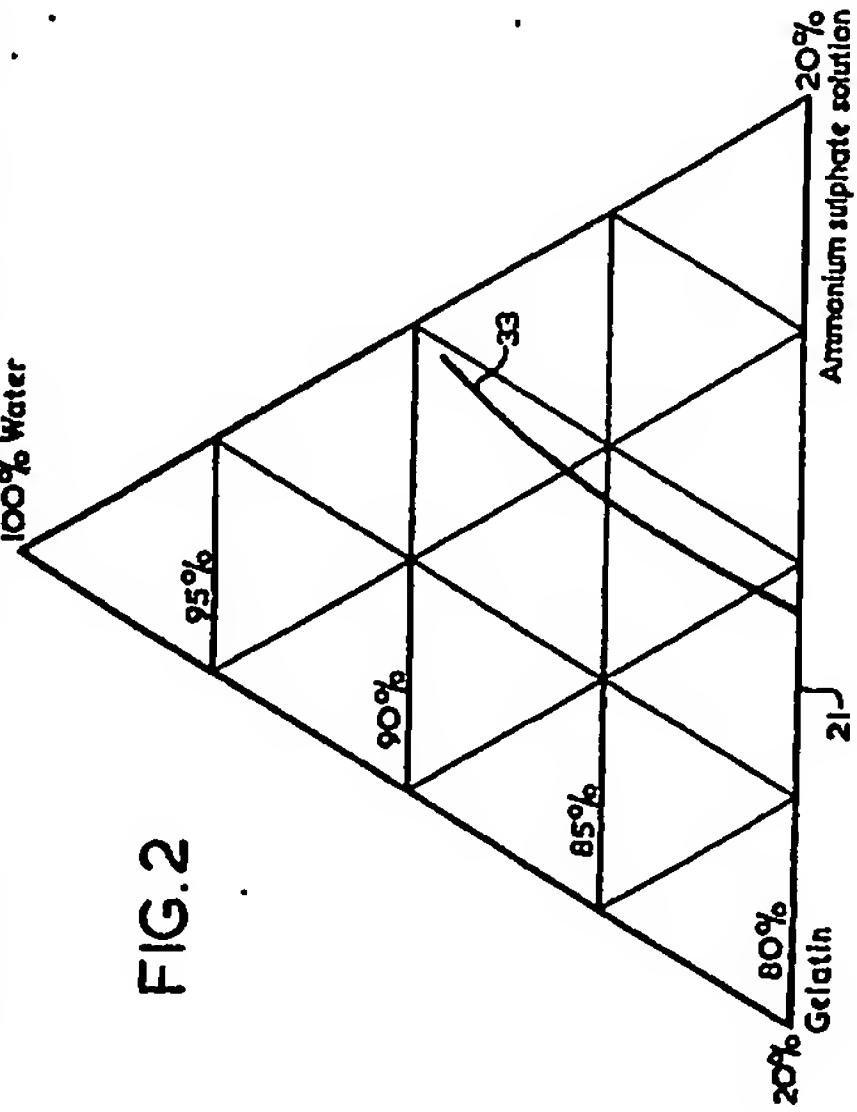
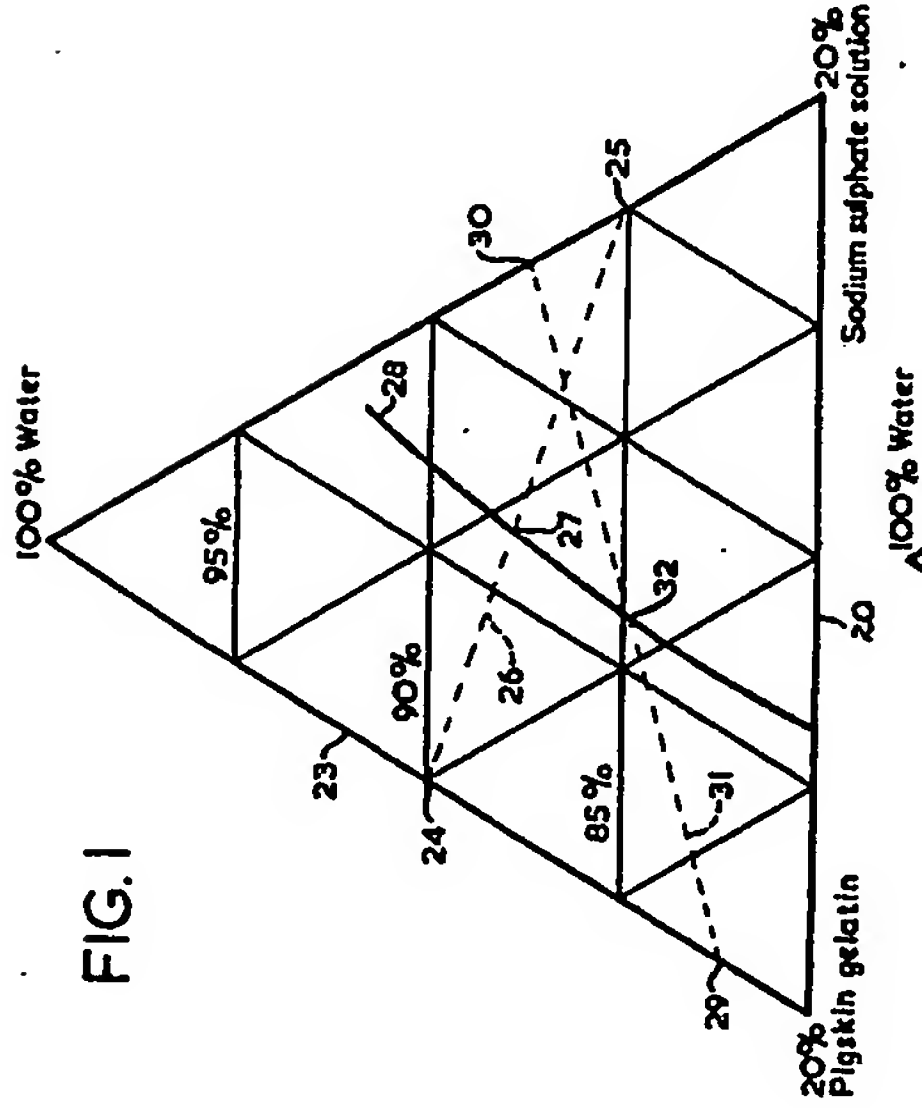


20%
e solution

FIG. 4



20%
solution



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.